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Observation of a Layered Structure of Polymer Langmuir−Blodgett Films by Transmission Electron Microscopy

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The Langmuir−Blodgett (LB) technique enables one to build up artificial layer structures of ultrathin films with a thickness of the molecular dimension.[1] Therefore, extensive studies on LB films have been made aiming toward the design and fabrication of electro- and photofunctional thin films.[2] Recently much attention has been paid to polymer LB films, because they may overcome the drawbacks of conventional fatty acid films which are associated with the poor thermal and mechanical stability.[3,4]

We have been studying poly(vinylalkanal acetal) as a representative of polymeric LB materials,[5,6] because the polymer bears excellent properties on the deposition process; it forms a stable monolayer on the water surface, which is successively deposited on a solid substrate as a two-dimensional form, and the transfer ratio of the monolayer onto various kinds of substrates is kept unity over a wide range of conditions. The obtained LB films show evidences that the deposition was successfully carried out layer by layer.[7]

Polymer scientists, however, often require some clear evidence for the layered structure because it is marvelous and interesting that a macromolecule being at a conformation of a three-dimensional random coil in solution can be rearranged into a two-dimensional planar form, resulting in a monolayer at the air−water interface. It is known that the small-angle X-ray scattering is useful for probing the periodic layer structure of crystalline LB films,[8] especially in the case of films containing heavy metals such as cadmium arachidate. Infrared spectroscopy is often used for measuring the orientation of molecules on the solid substrate.[9] But these are hardly applicable for studying LB films composed of flexible and amorphous polymers. Previously, we applied the energy transfer method to measure the layer-to-layer distance in the multilayer LB films of poly(vinylalkanal acetal)s and showed that each polymer layer was deposited with a thickness of monolayer as expected, but involving a partly disordered structure introduced by aging or by heating after the deposition.[10,11] We think that the energy transfer method using fluorescent probes provided clear evidence for the layered structure, but it is still desirable to perform direct observation of LB films by transmission electron microscopy (TEM).

In the current study for this purpose, we synthesized poly(vinylpentanal acetal) bearing unsaturated double bonds in the side chains, which are stainable with osmium tetraoxide, giving a contrast to the TEM photograph. In order to observe the cross section of the layered films, the specimen was sliced by an ultramicrotome and the projection was imaged by TEM.[12]

Experimental Part

Materials. Poly(vinylpentanal acetal) (PVP) was synthesized by the acetal reaction of pentanal and commercial poly(vinyl alcohol) (Wako Pure Chemical Industries, DP = 2000). Details have been described elsewhere.[5] To a part of the side chains of PVP was introduced *cis*-4-decenal (Aldrich) by mixing with pentanal during the acetal reaction.

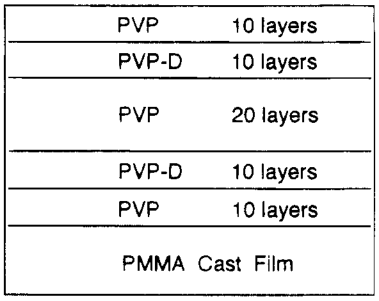

Figure 1. Layer structure of the prepared LB film on a PMMA substrate.

Table 1. Compositions of Poly(vinylalkanal acetal)s, Surface Pressures at the LB Deposition, and Glass Transition Temperatures (T_g) of the Bulk Polymer

sample	X (%)	Y (%)	$1 - X - Y$ (%)	surface pressure, (mN m^{-1})	T_g (°C)
PVP	66	0	34	17.0	54
PVP-D	48	12	40	16.5	42

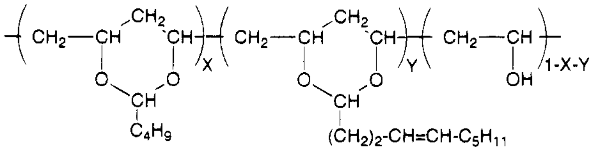

Table 1 shows the fraction of unsaturated unit and alkyl unit in the acetalized polymers. These fractions were determined by NMR, and the carbon fraction was measured by elementary analysis.

Sample Preparation. A dilute solution of the acetalized polymer (0.01 wt %) in benzene (Dojin, spectrograde) was spread onto the surface of pure water at 19 °C in a Teflon-coated rectangular trough (Kenkosha Model SI-1) equipped with a Wilhelmy-type film balance. The water was purified by deionization, distillation, and then passage through a water purification system (Barnstead Nanopure II). The monolayer was compressed to an appropriate surface pressure listed in Table 1, and then it was transferred vertically onto a poly(methyl methacrylate) (PMMA) film with a thickness of 120 μm which was beforehand prepared by casting from a benzene solution of PMMA. The deposition was performed with a transfer ratio around unity in both the up and down modes, yielding a Y-type LB film.

Figure 1 shows the prepared layer structures of the sample film. To fit the structural dimension with the spatial resolution of TEM, the LB films were made with a unit of 10 layers; i.e., the unit length of structure is 10 nm because the thickness per layer is known to be ca. 1 nm. The 20 layers of PVP (unstainable without unsaturated bonds) was sandwiched by 10 layers of PVP-D (stainable), and both sides of them were covered again with 10 layers of PVP films which were the precoating and protecting layers. Therefore, the sample film consists of a total of 60 layers.

The LB film on the thick PMMA film was first stained by exposure to osmium tetraoxide vapor for several hours and then buried in an epoxy resin which was cured at room temperature for a few days. The obtained epoxy block was trimmed as previously reported[12] and sliced by using an ultramicrotome (LKB 4800A Ultrotome) with a glass knife, yielding ultrathin sections of ca. 50 nm thickness.

Measurements. Electron microscopic observation was done with a Hitachi H-600 transmission electron microscope operated at 100 kV. The glass transition temperatures (T_g)

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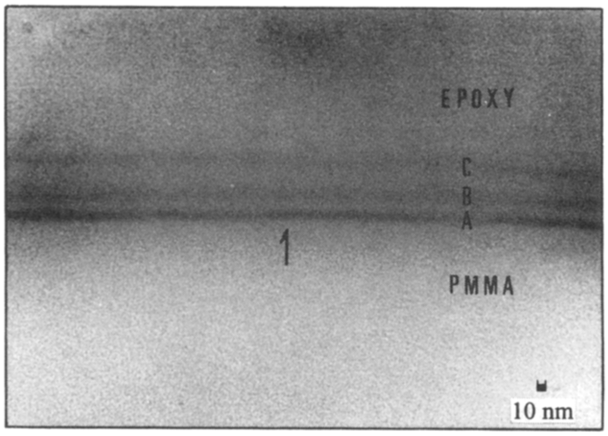

Figure 2. Transmission electron micrograph of ultrathin sections of PVP LB films stained by osmium tetraoxide.

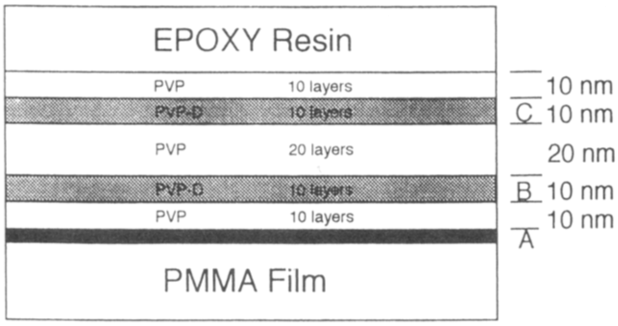

Figure 3. Schematic illustration of the structure seen in Figure 2.

of the prepared polymers were measured with a Mettler thermosystem Model FP-85.

Results and Discussion

Figure 2 shows a typical photograph obtained by TEM, in which three straight lines are seen at the interface between the PMMA (lower side) and epoxy resin (upper side). Figure 3 depicts a schematic illustration of the layer geometry. The thickest line (designated as A) among them is interpreted as the surface of the PMMA substrate on which the osmium vapor is strongly deposited due to an unknown reason. Besides this, a pair of thin parallel lines (designated as B and C) exists at the boundary. The spacing of these lines is obviously wider than the distance between the first thick (A) and the next thin (B) lines, indicating these thin lines are of the stained PVP-D LB films separated by the 20 layers of PVP film.

Figure 4 shows the darkness profile of the electron micrograph in the direction indicated by an arrow in Figure 2. Three dark lines in Figure 2 are clearly distinguished as the peaks in Figure 4. The widths of the peaks in Figure 4 are about 10 nm each and in good agreement with the expected thickness of 10 layers of PVP-D. The widths of the bright area between the peaks are about 10 and 20 nm, which remarkably agree with the expected thicknesses for the 10 and 20 nm layers of PVP, respectively. These results suggest that the deposition of the polymer molecules layer by layer as depicted in Figure 3 was successful.

The sample heated to 70 °C for 2 h before exposure to the osmium vapor was also investigated by TEM. The boundary between the PMMA and epoxy resin could be distinguished, but the LB films were hardly seen any more. The heating temperature was chosen from the T_g of polymers listed in Table 1. In the previous works studied by the energy transfer method, we have demonstrated that the critical temperature at which the disordering of the layered structure starts is closely related to the T_g measured for the corresponding bulk polymer.[11] Therefore, the temperature 70 °C is high enough to disorder the LB films but much lower than the T_g of the PMMA substrate (102 °C). As a consequence, the image of the LB films was gone from the photograph.

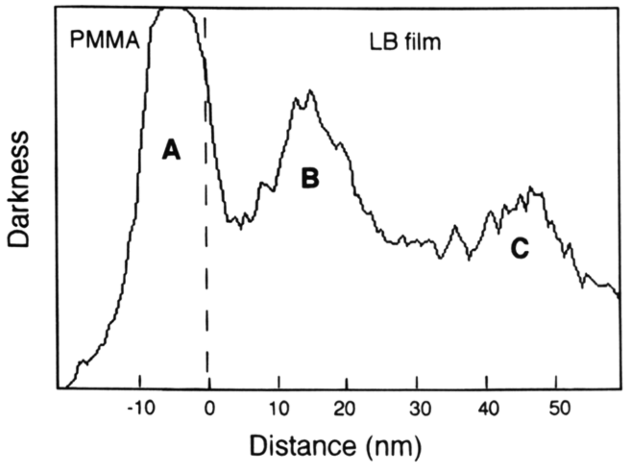

Figure 4. Darkness profile in the direction indicated by an arrow in Figure 2.

As to the origin of the unknown stripe A, we have no solution at the moment but are able to point out a few possibilities. First, some stainable contaminant may be introduced at the surface of the PMMA film on the casting or drying process. Another possibility is the different diffusivity of osmium vapor in the PVP LB and PMMA films. When exposed to the vapor, a lot of osmium may be accumulated and adsorbed at the surface of the less diffusive PMMA film.

In conclusion, we demonstrated the layered structure of polymer LB films by TEM pictures. The result was in good agreement with that previously shown by the energy transfer method, but the direct observation by TEM gave us clear features on the polymer LB films which could be stacked onto a substrate in a two-dimensional planar form, yielding polymer architectures in a nanometer dimension.

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